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Levels of trace elements in wetland waters and possible risk for plants: a case study of the Palo Laziale wood (central Italy)

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Abstract

The Palo Laziale wood represents one of the few remaining examples of Mediterranean wetland and it was identified as a Site of Community Importance (SCI) according to the European Commission Habitats Directive (92/43/EEC).
This paper reports levels of trace elements in wetland waters and possible risk for plants. Eight water points were sampled from private wells and analysed to investigate the distribution and enrichment of heavy metals in groundwater. In particular, Mn, Fe, Ni, Cu, Zn, As and Pb were analysed during four sampling events (from October 2010 to July 2011).
The results obtained show similar temporal variation of elements. Mn, Cu, Zn and As show major values during December, while Fe present major value during March. Pb concentration shows a peak during March, probably due a failure in water pipes.

Keywords: *Trace elements; risk assessment; groundwaters; Palo Laziale wetland system.*

Introduction

Wetland ecosystems are considered to be transitional areas between aquatic and terrestrial ecosystems [1]. The hydrology of a wetland is largely responsible for the vegetation of the wetland, which in turn affects the value of the wetland to animals and people. The duration and seasonality of flooding and [or] soil saturation, ground-water level, soil type, and drainage characteristics exert a strong influence on the number, type, and distribution of plants and plant communities in wetland. Because wetland often occurs in discrete patches within a matrix of upland habitat, many species of wetland-dependant organisms live in multiple populations that occasionally exchange individuals through migration, that is, in metapopulations [2, 3]. Local populations of wetland species often are small and isolated and thus vulnerable to extinction caused by change demographic event, disease, inbreeding [4, 5] or natural events, such as changing water levels, succession of wetland vegetation and habitat destruction [6, 7].

The Palo Laziale wood represents one of the few remaining examples of Mediterranean wetland and it is supported by a water table located near the surface and characterised by natural pond. This area is a good example of a coastal wetland system in central Italy. In June 1995, it was identified as a Site of Community Importance (SCI) according to the European Commission Habitats Directive (92/43/EEC). The motivation for this choice was the recognition of the good conservation status of the area as a representative of European community priority habitat category “3170* — Mediterranean temporary ponds” together with its importance for migratory birds and the rich fauna of arthropods and vertebrates characteristic of the hygrophilous wood [8]. The artificial withdrawal of water to irrigate the fields near the Palo Laziale wetland has changed the geochemical conditions of the aquifer

associated with the wetland the first evidence of stress on the area's tree species was detected at the end of 1995 [8].

The trees showing these effects belonged primarily to the genus Quercus. Visible signs of increasing tree mortality became evident during the following years. This process has continued until the present and has caused the complete collapse of the forest habitat, with the deaths of more than 4000 individual trees. The low specificity of these symptoms, together with the many single causal factors proposed to explain the decline of ecosystem in various parts of Europe [9, 10, 11, 12, 13], suggest that oak decline can be attributed to several different site-specific factors and/or that the decline may involve a succession of several abiotic and biotic factors [14, 15]. Also wetlands are recognized to be important sinks as filters, retaining heavy metals that can have toxic effects on biota. Heavy metals are natural elements that are found at various high background levels at different places throughout the world, due to various concentrations in the bedrock. Generally, they are persistent and cannot be deleted from the environment. Thus, a problem arises when their availability is high due to high background levels or human activity. The aim of this paper is to investigate the distribution and enrichment of trace metals in groundwater.

Study area

The study area is located in the town of Ladispoli, approximately 50 km north of Rome, in central Italy on the south-eastern coast of the Tyrrhenian Sea (**Fig. 1**).
The climate is Mediterranean, with cool, wet winters and warm to hot, dry summers. The average annual rainfall is 733 mm. This rainfall occurs primarily during the winter. The present lithology of the area consists of alternating alluvial and deltaic sediments and it is represented by [8]:
1. Sandy shore
2. Current and recent flood sediments: peaty clays and black marshlands;
3. Conglomerates of Palidoro: conglomerates with large constituent grains;
4. Conglomerates of Fosso Vaccina: pudding stones and polygenic pebbles, with large and medium-sized elements, free of volcanic pebbles.

The Pliocene and Quaternary deposits of the area rest on a sediment substrate consisting of pelites [blue clays, marly clays and blue-grey marl]. This substrate is crucial in hydrological terms because it forms the impermeable base that supports the regional aquifer. It is located in volcanic deposits and in marine and continental sediments [16]. Groundwater occurs at an average depth of 2 m below the surface. The flow system is controlled by the topography. The dominant flow occurs from the higher topographic area in the northeast towards the area of lower topography in the southwest [16]. Variations in the hydraulic gradient are related to the spatial characteristics of the aquifer and the presence of wells.

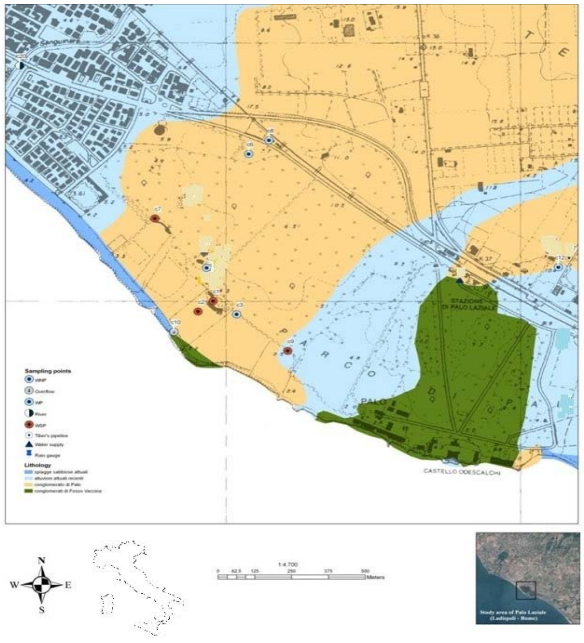

Figure 1: Study area and water points localization.

Sampling and analytical techniques

The geochemistry and the evolution of the aquifer of the Palo Laziale wetland system was investigated by sampling from private wells used for agricultural water supply in the area (**Figure 1**) with a total of 8 water points. Samples c8 and c12 are located outside the Palo wood, while others samples are located inside it. The sampling was performed from October 2010 through July 2011. All samples were collected in laboratory certified clean bottles and labelled as to the well depth and location, date and time of sample collection, analyses to be performed, and field preservation performed, if any [17]. Concentrations of minor and trace elements were measured using an ICP-MS (X Series 2 Thermo Fisher Scientific) following filtration (0.45 μm) and acidification in the field (HNO_3 1:1). The analyses were performed at the Geochemical Laboratory of Sapienza, University of Rome (Italy). The analytical accuracy of these methods ranged from 2% to 5%. An internal standard, Rh, was used to correct the ICP-MS instrumental drift. Ultrapure water (Millipore, Milli-Q, 16 MΩ cm) was used in preparing blanks, standard solutions, and sample dilutions.

Results and Discussions

Minor elements for groundwater samples of study area were reported in **Table 1.**

October 2010		Mn	Fe	Ni	Cu	Zn	As	Pb
	c1	24.7	3.20	5.77	1.34	5.64	2.13	0.30
	c2	13.9	2.20	3.67	0.37	1.63	1.50	0.30
	c3	6.20	2.90	7.01	2.16	5.65	0.74	0.20
	c5	28.0	3.40	2.28	0.67	2.89	2.24	0.20
	c7	9.30	5.50	0.49	0.23	7.50	1.66	0.20
	c8	2.00	2.00	0.13	1.66	2.23	4.24	0.20
	c9	0.30	3.30	0.41	0.58	2.32	1.87	0.20
	c12	106	90.0	0.62	0.64	3.32	3.60	1.10
	Mean	*23.8*	*14.1*	*2.55*	*0.96*	*3.90*	*2.25*	*0.34*
December 2010	c1	12.7	14.6	4.88	1.59	23.6	1.32	4.50
	c2	31.6	34.7	7.96	14.5	34.4	2.93	7.30
	c3	2.70	57.4	7.08	4.78	9.17	3.06	24.0
	c5	23.5	14.5	3.69	2.91	43.4	3.06	11.5
	c7	409	19.0	3.70	3.08	35.0	3.78	0.50
	c8	0.90	24.2	0.83	154	30.0	8.83	1.20
	c9	16.1	17.4	1.33	8.16	18.0	4.21	28.4
	c10	18.7	7.40	7.51	0.91	4.80	2.91	4.50
	c12	238	102	1.17	1.10	3.43	7.41	0.40
	Mean	*83.7*	*32.33*	*4.24*	*21.17*	*22.40*	*4.17*	*9.14*
March 2011	c1	17.3	108	4.18	5.51	8.69	1.97	11.9
	c2	41.8	8.20	7.21	0.89	1.88	2.81	15.4
	c3	6.30	97.5	7.43	2.17	6.94	1.67	36.9
	c5	125	8.90	3.75	1.16	4.26	2.07	7.60
	c7	37.7	8.30	1.28	1.01	41.3	2.34	0.20
	c8	1.70	9.20	0.66	1.28	41.2	5.61	0.50
	c9	6.90	114	1.66	2.87	11.3	2.27	95.7
	c10	12.7	6.10	5.90	0.68	1.13	2.30	2.00
	c12	114	192	2.62	7.50	19.1	4.31	305
	Mean	*40.4*	*61.3*	*3.85*	*2.56*	*15.1*	*2.82*	*52.8*
July 2011	c1	106	6.80	10.0	2.04	8.87	3.38	0.80
	c2	45.0	7.70	7.98	0.83	3.75	2.08	0.20
	c3	57.3	9.50	10.3	1.24	5.62	1.60	0.30
	c5	9.80	5.50	3.03	0.72	8.28	2.47	0.60
	c7	41.2	3.00	0.59	0.45	4.74	2.67	0.90
	c9	0.20	8.00	0.84	1.03	3.65	2.78	0.50
	c10	0.80	2.40	6.76	0.74	3.84	2.14	0.70
	c12	0.40	19.9	0.55	1.61	6.18	2.53	0.90
	Mean	*32.6*	*7.85*	*5.01*	*1.08*	*5.62*	*2.46*	*0.61*
Statistical parameters	*Max.*	*409*	*192*	*10.3*	*154*	*43.4*	*8.83*	*305*
	Min.	*0.20*	*2.00*	*0.13*	*0.23*	*1.13*	*0.74*	*0.20*
	Mean	*46.4*	*30.4*	*3.89*	*6.88*	*12.3*	*2.97*	*17.0*

Table1: Elements concentrations in groundwater analysed during 4 sampling events. The values are expressed in µg/L

It shows elements concentrations for each sampling event and minimum, maximum and mean values of total measures. Particularly, Mn, Fe, Ni, Cu, Zn, As and Pb were analysed during four sampling events (from October 2010 to July 2011). Figure 2 shows the wetland time-series results for the trace elements determined in the water samples.

The figures group of these elements into sets showing similar temporal behaviour.

Mn values range between 0.20 and 409 µg/L, while Fe concentrations range from 2.0 to 192 µg/L.

These elements show a large seasonal variation (**Figure 2**):

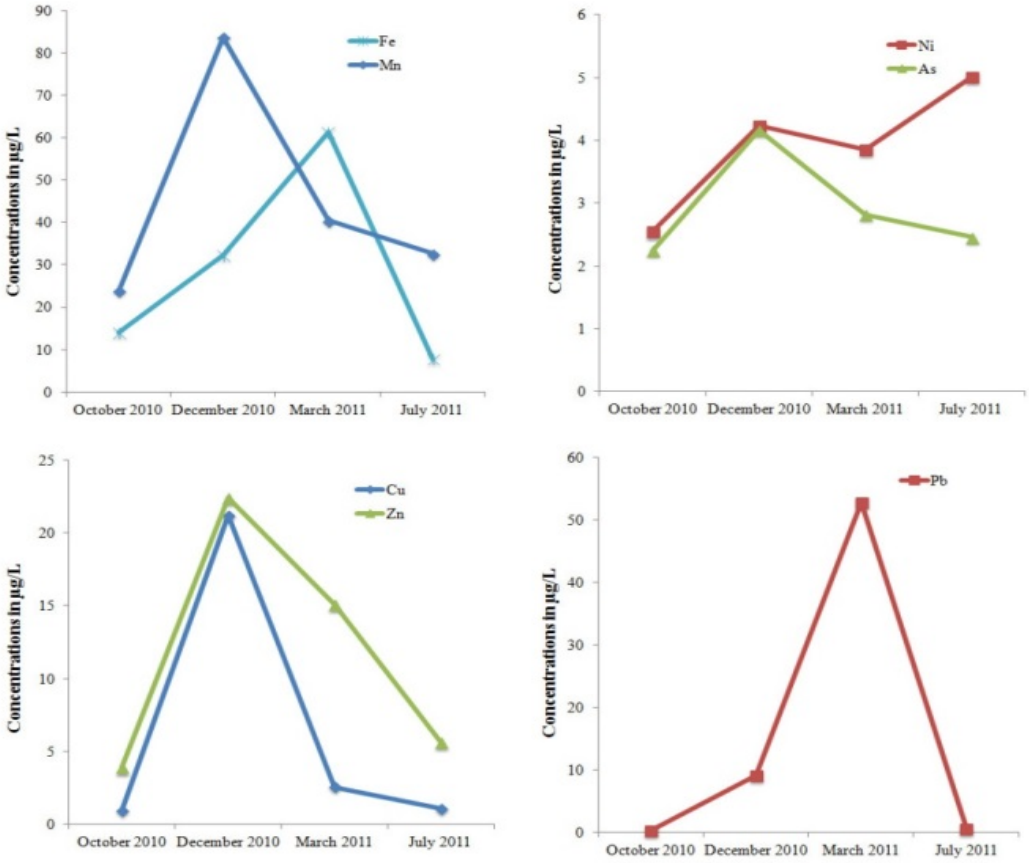

Figure 2: Temporal variation of trace elements analysed.

Mn mean values presents a peak in December while Fe shows the highest mean value in March respectively in sample c7 and c12. Both elements show lower concentrations during October and July.

Manganese (Mn) is an essential micronutrient in most plants. Its deficit is dangerous for chloroplasts because it affects the water-splitting system of photosystem II (PSII), which provides the necessary electrons for photosynthesis [18]. However, its excess seems also to be particularly damaging to the photosynthetic apparatus [19]. Excessive Mn concentrations in plant tissues can alter various processes, such as enzyme activity, absorption, translocation and utilization of other mineral elements (Ca, Mg, Fe and P), causing oxidative stress [20, 21]. The threshold of Mn injury as well as the tolerance to an excess of this metal is highly dependent on the plant species and cultivars or genotypes within a species [22, 23].

Iron concentrations are generally small in water. The chemical behaviour of iron and its solubility in water depend strongly on the oxidation intensity in the system in which it occurs. Also, it is an essential element in the metabolism of animals and plants. In particular, there is some evidence that high iron concentrations may influence the growth and distribution of various wetland plant taxa [24, 25].

For this reason, iron determinations are commonly included in chemical analyses of water.

Manganese is not an essential constituent of any of the more common silicate rock minerals, but it can substitute for iron, magnesium, or calcium in silicate structures. The chemistry of manganese is somewhat like that of iron in that both metals participate in redox processes in weathering environments [26]. Both elements can derive by litologhy of study area, particularly by clay that form the substrate and the peak concentrations measured in winter, especially for Mn which reaches a value of 409 µg/L, could be attributed to the corrosion of pump parts.

Cu and Zn also present the same trend of Mn, with a peak concentration during December (**Figure 2**). Cu concentrations range between 0.23 to 154 µg/L, while Zn values were between 1.13 and 43.4 µg/L. Copper may occur in solution in either Cu^{2+} or Cu^{+} oxidation states, but the redox conditions in oxygenated water and the tendency of Cu^{+} ions to disproportionate favor the more oxidized for [26]. Copper salts are sometimes purposely added in small amounts to water-supply reservoirs to suppress the growth of algae. Organic and inorganic compounds of copper have been used extensively in agricultural pesticide sprays. This heavy metal is an indispensable component of oxidative enzymes or of particular structural components of cells. However, overdosed copper has a strong toxic effect on plant. In sensitive forms of higher plants, excess Cu causes various effects depending strongly, among other things, on the plant growth stage at which the metal was applied and on the time of its action.

Excess Cu applied at the initial growth stage strongly inhibits leaf expansion and increases content of pigments calculated per leaf area unit [27, 28] rocks as copper and is thus fairly common.

Zinc has only one significant oxidation state, Zn^{2+}, and tends to be substantially more soluble in most types of natural water than are the other two metals [26]. Like Cu, Zn is an essential metal to higher plants and is involved in several important metabolic processes. It activates enzymes or is incorporated into metallo-enzymes in the electron transport system. Further, Zn plays an important role in the protein synthesis, as in the carbohydrate, nucleic acid and lipid metabolism. As Zn forms stable complexes with DNA and RNA it might also affect DNA and RNA stability [29]. A deficiency of Zn in plants may cause significant changes in the plant metabolism, resulting in growth retardation, stunted growth and chlorosis.

Ni and As present same trend during October and December (see **Figure 2**) with mean values about 2 and 4 µg/L. In March, Ni concentration undergoes a slight reduction, but increased again in July, while As decrease from December to July. According to Latimer (1952) [30] the aqueous chemistry of nickel is primarily concerned with the Ni^{2+} oxidation state. Solid species for which thermodynamic data are given by Latimer include the Ni^{4+} oxide NiO_2 and the hydroxide species $Ni(OH)_3$.

Ni is an essential element for plants, but it is toxic if present in high concentration. Plant tolerance to nickel (Ni) toxicity depends on plant differences for uptake and distribution within tissues; Ni toxicity gives rise to chlorosis of the leaves in many species. Leaves showing Ni-induced chlorosis are found to contain sub-optimal levels of Fe (31, 32); in some cases Ni-induced chlorosis may be alleviated by foliar applications of $FeS0_4$ [32], suggesting an effect of Ni on the translocation of Fe [33, 34].

Because small amounts of arsenic can be toxic to humans, this element is considered a highly undesirable impurity in water. The stable forms of arsenic in solution in water are arsenate (AsV) and arsenite (AsIII) oxyanions. Arsenic has been used as a component of pesticides and may thus enter streams or groundwater through waste disposal or agricultural drainage. An important factor in the natural circulation of arsenic, however, is the volatility of the element and some of its compounds [26]. Arsenic can be potentially toxic also to low concentrations. It may form metal arsenides in which its oxidation state is negative. Arsenic may also form sulfides and can be present as an accessory element in sulfide ore deposits.

Pb is not known to be essential for the growth of plants, but the most confusing aspect of Pb toxicology is the lack of any consistent relationship between amounts of Pb in the soil and the extent of the toxicity. Lead gives rise to a wide range of toxicity symptoms in plants such as root elongation is inhibited. Anyway, Pb concentration in our samples ranged between 0.20 to 305 µg/L. The highest value was measured during March 2011 in samples c12, located outside of the study area. Possible anthropogenic sources of lead in groundwater are water pipes [35]. Pb concentration is high only in sample c12 and only during March, therefore it could be due a locally problem in water pipes. The Latin word for lead, "plumbum," is preserved in the English terms relating to water conveyance ("plumbing," etc.) and suggest the long history of the use of lead for water pipes. The principal dissolved inorganic forms of lead are the free ion Pb^{2+}, hydroxide complexes, and, probably, the carbonate and sulfate ion pairs. The importance of organic complexes is uncertain, but they may constitute a significant part of the dissolved lead in some waters.

Conclusions

This paper shows levels of some trace elements in wetland waters of Palo Laziale wood and it considered possible risk for plants. The Palo Laziale wood represents one of the few remaining examples of Mediterranean wetland and it is supported by a water table located nearthe surface and characterised by natural pond. This

area is a good example of a coastal wetland system in central Italy. In June 1995, it was identified as a Site of Community Importance (SCI) according to the European Commission Habitats Directive (92/43/EEC).

Were investigated concentrations of some elements as: Mn, Fe, Ni, Cu, Zn, As and Pb and were considered the temporal behaviour and their effects on the plants. Mn, Ni, Cu, Zn and As show higher values during December, while Fe reaches major concentration during March. However, none of these values suggest contamination phenomenon and risks for plants. Pb values show a peak concentration during March in a sample located outside the Palo wood. Probably this value is due a failure in water pipes.

The hydrology of a wetland is largely responsible for the vegetation, which in turn affects the value of the wetland to animals and people, therefore the monitoring of groundwater chemistry, particularly of trace elements, is very important.

References

1. Brinson MM. Changes in the functioning of wetlands along environmental gradients. Wetlands, 1993, (13):65–74.
2. Levins R. 1970. Extinction. *In* M. Gerstenhaber (ed.) Some Mathematical Problems in Biology. American Mathematical Society, Providence, RI, USA, 1970: 77–107.
3. Hanski I and Gilpin ME. Metapopulation dynamics: brief history and conceptual domain. Biological Journal of the Linnean Society, 1991, (42): 3–16.
4. Møller TR and Rørdam CP. Species numbers of vascular plants in relation to area, isolation and age of ponds in Denmark, Oikos, 1985, (45): 8–16.
5. Dodd CK. Effects of habitat fragmentation on a streamdwelling species, the flattened musk turtle*Sternotherus depressus*. Biological Conservation, 1990, (45): 33–45.
6. Gill DE. 1978. The metapopulation ecology of the red-spotted newt, *Notophthalmus viridescens* (Rafinesque). Ecological Monographs, 1978, (48): 145–166.
7. Naiman RJ, Johnston CA, Kelley JC. Alteration of North American streams by beaver. Bio Science, 1988, (38): 753–762.
8. Barbieri M, Battistel M, Garone A. The geochemical evolution and management of a coastal wetland system: A case study of the Palo Laziale protected area. Journal of geochemical exploration, 2013, (126-127): 67-77.
9. Brasier CM, Robredo F, Ferraz JFP. Evidence for Phytophthora cinnamomi involvement in Iberian oak decline. Plant Pathology, 1993, (42): 140–145.
10. Hartmann G and Blank R. Winterfrost, Kahlfrass und Prachtkäpferbefall als Faktoren im Ursachenkomplex des Eichensterbens in Norddeutschland. Forst und Holz, 1992, (47): 443–452.
11. Jung T, Blaschke H, Oßwald W. Involvement of soilborne Phytophthora species in Central European oak decline and the effect of site factors on the disease. Plant Pathology, 2000, (49): 706–718.
12. Siwecki R. and Ulfnarski K. Review of oak stand decline with special reference to the role of drought in Poland. European Journal of Forest Pathology, 1998, (28): 99–112.
13. Thomas FM and Hartmann G. Tree rooting patterns and soil water relations of healthy and damaged stands of mature oak (Quercus robur L. & Quercus petraea [Matt.] Liebl.). Plant and Soil, 1998, (203): 145–158.
14. Manion PD. Tree Disease Concepts. Prentice Hall Inc., Englewood Cliffs, NJ. USA, 1991.
15. Thomas FM, Blank R, Hartmann G. Abiotic and biotic factors and their interactions as causes of oak decline in Central Europe. Forest Pathology, 2002, (32): 277–307.
16. Ventriglia. Idrogeologia della Provincia di Roma. Regione Tolfetana, vol. I, 1988.
17. APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater (18th edn) American Public Health Association, Baltimore, MD, 1992.
18. Buchanan B, Grusen W, Jones R. Biochemistry and molecular biology of plants. American Society, of Plant Physiologists Maryland, 2000: 1367 p.
19. Mukhopadhyay M and Sharma A. Manganese in cell metabolism of higher plants Bot. Rev. 1991, (57): 117-149.
20. Ducic T. and Polle A. Transport and detoxification of manganese and copper in plants. Braz. J. Plant Physiol. 2005, (17): 103-112.
21. Lei Y, Korpelainen H, Li C. Physiological and biochemical responses to high Mn concentrations in two contrasting Populus cathayana populations. Chemosphere, 2007, (68): 686-694.
22. Foy C, Scott B, Fisher J. Genetic differences in plant tolerance to manganese toxicity. In: R.D. Graham, R.J. Hannam, N.J. Uren. (eds). Manganese in Soil and Plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988: 293-307.
23. Horst WJ. The physiology of manganese toxicity. In: R.D. Graham, R.J. Hannam, N.J. Uren (eds). Manganese in Soil and Plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988: 175-188.

24. Tanaka AA, Kawano K, Yamaguchi J. Photosynthesis, respiration, and plant type of the tropical rice plant. I. R.R. I. Tec. Bull. 7, Philippines, 1966.
25. Al-Farraj MM. The Influence of Environmental Conditions on the Growth of Wetland Plants, with Special Reference to Epilobium Hirsutum L. and E. Palustre L. 1983.
26. Hem JD. Study and interpretation of the chemical characteristics of the natural water (3d ed.). U.S. Geological Survey Water-Supply paper, 1989.
27. Maksymiec W, Baszynski T, Bednara J. Responses of runner bean plants to excess copper as a function of plant growth stages: Effects on morphology and structure of primary leaves and their chloroplast ultrastructure. Photosynthetica, 1995.
28. Maksymiec W, and Tadeusz Baszyński T. "Chlorophyll fluorescence in primary leaves of excess Cu-treated runner bean plants depends on their growth stages and the duration of Cu-action." Journal of Plant Physiology 1996: 196-200.
29. Collins JC. *In* Lepp, N. W. (ed.), Effect of Heavy Metal Pollution on Plants, Vol. 1. Applied Science Publishers, London and New Jersey, 1981: 145.
30. Latimer WM. Oxidation potentials (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, 1952: 392.
31. Nicholas DJD, Lloyd-Jones CP, Fisher DJ. Some problems associated with determining iron in plants. Plant Soil, 1957, (8): 367-77.
32. Roth JA, Wallihan EF, Sharpless RG. Uptake by oats and soybeans of copper and nickel added to a peat soil. Soil Sci, 1971, (112): 338-342.
33. Hewitt EJ. Metal interrelationships in plant nutrition. 1. Effects of some metal toxicities in sugar beet, tomato, oat, potato, and narrowstem kale grown in sand cultures. J Exp Bot, 1953, (4): 59-64.
34. Lingle JC, Tiffin LO, Brown JC. Iron uptake-translocation of soybeans as influenced by other cations. Plant Physiol, 1963, (38): 71-76.
35. Wallace A, De Kock PC. Translocation of iron in tobacco, sunflower and bush bean plants. In: Wallace A (ed) Current topics in plant nutrition. Calif Agr, 1966.
36. Lasheen MR, Sharaby CM, El-Kholy NG, Elsherif IY, El-Wakeel ST.Factors influencing lead and iron release from some Egyptian drinking water pipes. Journal of Hazardous Materials,2008,(160):675-680.